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THE MAGNETIC AND ELECTRIC MEASUREMENTS OF THE MULTIFERROIC $PbFe_{1/2}Nb_{1/2}O_3$ CERAMICS OBTAINED USING HOT UNIAXIAL PRESSURE METHOD

We present the results of investigations of $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramic samples obtained using two-step synthesis (i.e. columbite method). For obtained samples complex investigations of microstructure, magnetic and electrophysical properties have been performed at low and at high temperatures. Microstructure is characterized by small grains with high homogeneity and high density (low porosity). Impedance of samples and the phase shift angle have been measured using LCR Meter. Next the AC electric conductivity, dielectric permittivity and loss tangent have been calculated. AC conductivity at frequency 3 Hz was measured in similar way using Quantum Design PPMS System in magnetic fields 1000 Oe and 10000 Oe. At temperature range 240K-260K the anomalies of conductivity are observed. These anomalies depend on measuring cycle (heating, cooling) and magnetic field.
Keywords: multiferroics, relaxor materials, magnetoelectric transducers

1. Introduction

Electronic components built on the basis of ceramic materials with the multiferroic properties due to their specific properties are never and have more versatile use in modern microelectronics and micromechatronics [1] especially in the form of nanomaterials and thin films [2-3]. In [4] multiferroicity is described as the coupling between magnetic and polarization orders. An example of another papers concerning multiferroicity can be [5-7]. One of the ceramic materials with a wide range of application is ferroelectromagnetic ceramic $PbFe_{1/2}Nb_{1/2}O_3$ (PFN). In last years the renaissance of magnetoelectric multiferroics is observed [8] as well as revival of the interest in magnetoelectric effect [9].

$Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) belongs to the biferroic materials. According to classification of Khomskii [10] PFN belongs to single phase 1-st type mutiferroics. Another example of 1-st type multiferroic can be solid solution BFN-BT [11]. Some symmetry aspects of ferroics and single phase multiferroics are presented in [12]. Undoped PFN exhibits simultaneously ferroelectric and antiferromagnetic properties below 143K. At the temperatures range from 143K to 388K this material is a relaxor ferroelectric. PFN has been obtained and described as ferroelectric first by Smolensky [13] in the fifties of the previous century. The structure of PFN is perovskite type. The elementary cell contains Fe^{3+} ions and Nb^{5+} in B-positions, while Pb^{2+} ion occupies A-positions [14]. According to relatively easy process of synthesis, low temperatures of sintering, low reactivity and high value of dielectric permittivity, PFN is still an attractive material for commercial electroceramics [15]. The main problem during obtaining PFN ceramics is formation of the second non-perovskite phase (pyrochlore phase) and related with this the high value of dielectric loss and high electric conductivity. It decreases the possibility of wide applications of this material in the electronic devices. It is possible to reduce these negative phenomena by doping PFN, for example by lithium [16-17], manganese or chromium [18].

In PFN ceramics a diffused para-ferroelectric transition at 370K-380K which exhibit behaviours typical for relaxor transitions and a para-antiferromagnetic transition at 145K have been observed (Neel temperature). At room temperature, in spite of high electric conductivity *P-E* dielectric hysteresis loop can be observed with remnant polarization of 11.5 $\mu C/cm^2$ and a coercive field of 4.04 kV/cm. Anomalies in the dielectric constant and loss tangent have been observed also around the temperature of 145K, indicating a coupling between the ferroelectric and antiferromagnetic orders in PFN ceramics [19]. X-ray and synchrotron investigations of PFN are described in [20].

Frequency-temperature response of PFN ceramics obtained by different precursors and dielectric relaxation near the transition temperature is described in [21].

Reliability and stability of the time parameters of electronic elements made on the basis of the PFN depends on the used method of obtaining, parameters of technological process, repeat-

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ability and an efficient way of polarization of ceramic samples e.t.c. In this work we present the results of obtaining of ceramic samples of PFN using two stage method of synthesis and hot pressing method of densification. Complex investigations of magnetic and electrophysical properties of obtained samples have been performed at low and at high temperatures.

2. Experiment

Our $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) ceramic samples have been obtained using two-step synthesis (i.e. columbite method). In the first step the $FeNbO_4$ was synthesized from a mixture of the oxides: Fe_2O_3 (99% purity) and Nb_2O_5 (>99.9% purity) at following conditions: T_{synth1} = 1273K, t_{synth1} = 4 h. In the second step the PFN powders were obtained from a mixture $FeNbO_4$ and PbO oxide (>99% purity) at following conditions: T_{synth2} = 1073K and t_{synth2} = 3 h. Densification of ceramics was conducted using hot uniaxial pressing method (HUP) with the following conditions: T_s = 1273K/t_s = 1 h/p_s = 20 MPa. The exact description of the technological process is presented at the previous works [22-23]. In [24] the relations between physical properties of the biferroic $Pb(Fe_{1-x}Nb_x)O_3$ ceramics and their composition change are presented.

XRD test of crystallographic structure was carried out using Philips X'pert diffractometer at room temperature (CuK_α radiation). The microstructure was tested using SEM HITACHI S-4700 scanning microscope. Impedance of samples and the phase shift angle have been measured using QuadTech 1920 precision LCR Meter during heating cycle (within the temperatures range from 100K to 475K at frequencies from 20 Hz to 10 kHz). Basing on the results of these measurements the AC electric conductivity, dielectric permittivity and loss tangent have been calculated. AC conductivity at frequency 3 Hz with amplitude U_{AC} = 5 V was measured in similar way using Quantum Design PPMS (Physical Property Measurement System) platform (from 3K to 300K) using four-probe method. $R(T)$ dependences were measured in magnetic fields 1000 Oe and 10000 Oe.

Ferroelectric hysteresis $P(E)$ loops have been obtained using Sawyer-Tower circuit and high voltage amplifier (Matsusada Inc. HEOPS-5B6). The data were stored on a computer disc using an A/D, D/A transducer card.

3. Results and discussion

X-ray diffraction pattern for the investigated PFN ceramics measured at room temperature is presented in Fig. 1. Obtained XRD pattern has been compared with the patterns of the PFN regular phase symmetry (JCPDS 00-032-0522), tetragonal symmetry (JCPDS 04-009-5124), rhombohedral symmetry (JCPDS 01-073-2022) and monoclinic one (JCPDS 04-014-5440). The best fit of the obtained results has been achieved for tetragonal symmetry (P4 mm space group). The XRD investigations have shown, moreover, that the observed diffraction maxima correspond to perovskite-type structure without foreign (pyrochlore) phase.

Fig. 2 shows the SEM image of the microstructure of PFN ceramic sample. Microstructure of the PFN ceramics

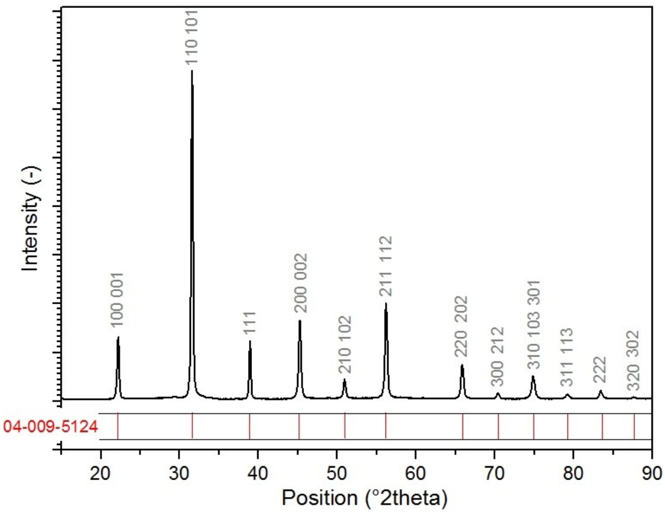

Fig. 1. X-ray diffraction pattern for the investigated PFN ceramics

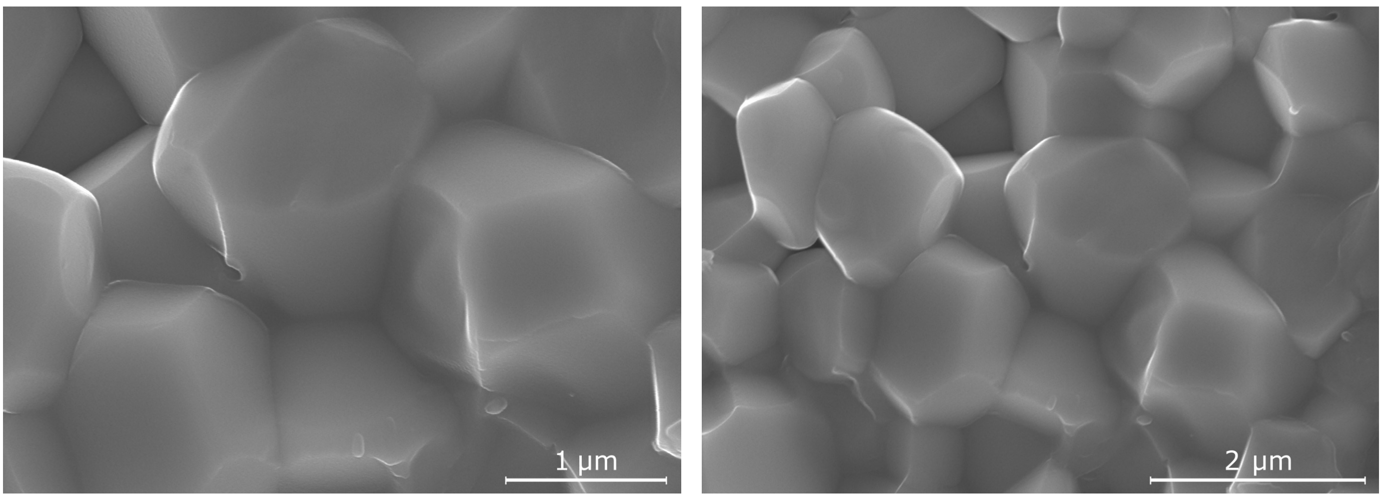

Fig. 2. SEM microstructure of the PFN ceramics

obtained by HUP method is characterized by small grains with high homogeneity and high density (low porosity). The grains are correctly formed and average grain size is smaller than 1.3 μm.

Temperature dependence of field cooled (FC) magnetization measured in field of 1 T for PFN ceramics is presented in Fig. 3. An anomaly (weak and broad maximum in the temperature range from 145K to 175K) observed on the temperature dependencies of the magnetization (in field cooled (FC) recorded in field of 1 T) corresponds to Neel temperature of investigated material. The $\mu(\mu_0 H)$ magnetic hysteresis of the PFN ceramics at temperature 10K (Fig. 3 inset) reveals the presence of weak ferromagnetic behavior below 10K. It is also seen from the inset in Fig. 3 that at temperature 100K the $\mu(\mu_0 H)$ dependency is linear. Results presented in Fig. 3 are similar like in [25].

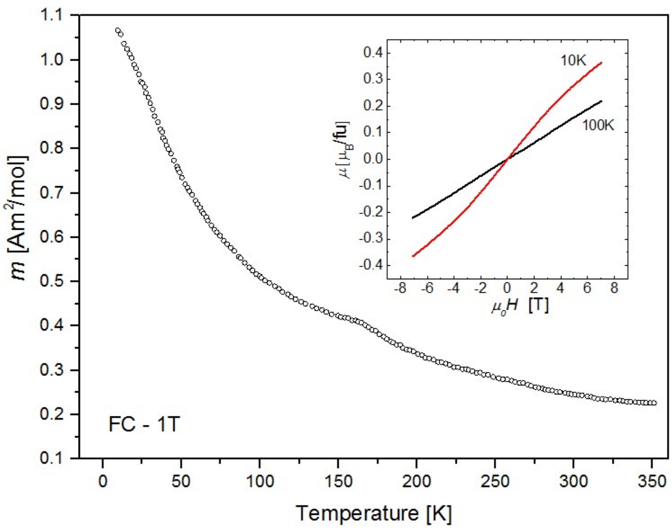

Fig. 3. Temperature dependence of field cooled (FC) magnetization recorded in field of 1 T for PFN ceramics [22]

The results of studies of temperature dependencies of AC electric conductivity of investigated PFN ceramics are presented in Fig. 4.

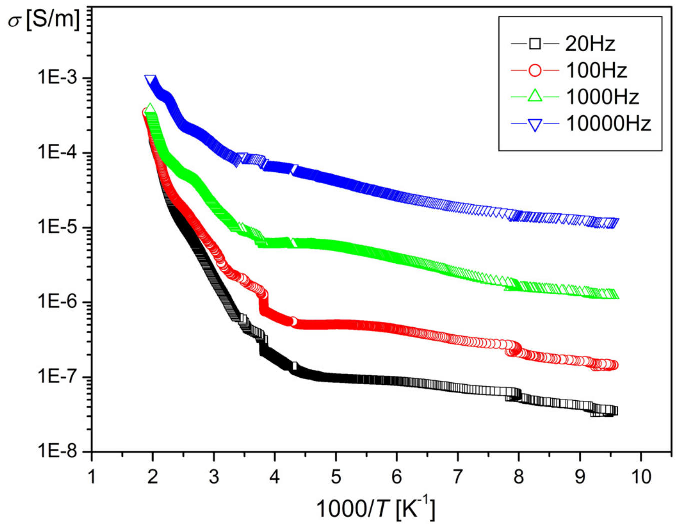

Fig. 4. Temperature dependence of the AC conductivity for the PFN ceramics (amplitude $U_{AC} = 1$ V)

For the lowest frequencies of the measuring field at temperature range 240K-260K the anomalies of conductivity are observed. These anomalies depend on measuring cycle (heating, cooling) and constant magnetic field what is presented in Fig. 5. Within the range 220-260K abrupt change of the slope lnσ(1000/T) is not observed but a gradual reduction instead.

From Fig. 5a and Fig. 5b it is also seen that in the temperature range from 225K to 255K the occuring anomaly (maximum of dependency lnσ(1000/T)) is observed which depends on the magnetic field. In general the higher magnetic field is applied to the sample the higher is the observed maximum of the anomaly.

Temperature dependencies of dielectric permittivity and tangent of angle of dielectric loss for PFN ceramics are presented in Fig. 6a and Fig. 6b respectively.

With the increase in frequency of the measuring field the values of the permittivity decrease. Diffused maxima of dielectric permittivity are observed at temperature T_m about 380K (the value of the maximum of dielectric permittivity ε_{max} at temperature T_m is equal to 5000-12000 depending on frequency). At the

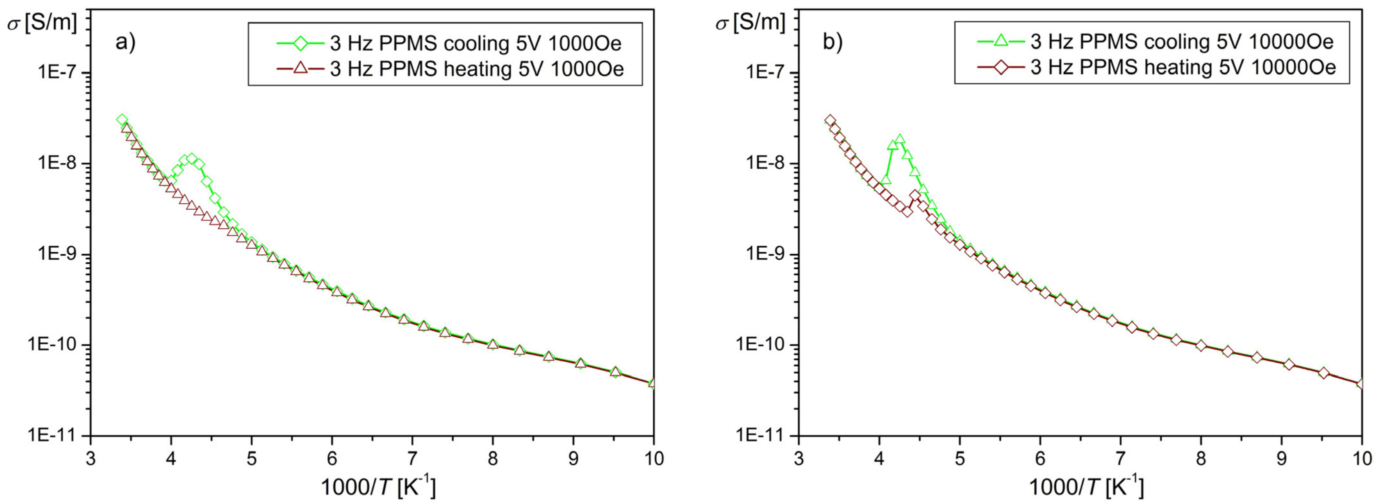

Fig. 5. Dependencies lnσ(1000/T) depending on measuring cycle (heating, cooling) and constant magnetic field for the PFN ceramics

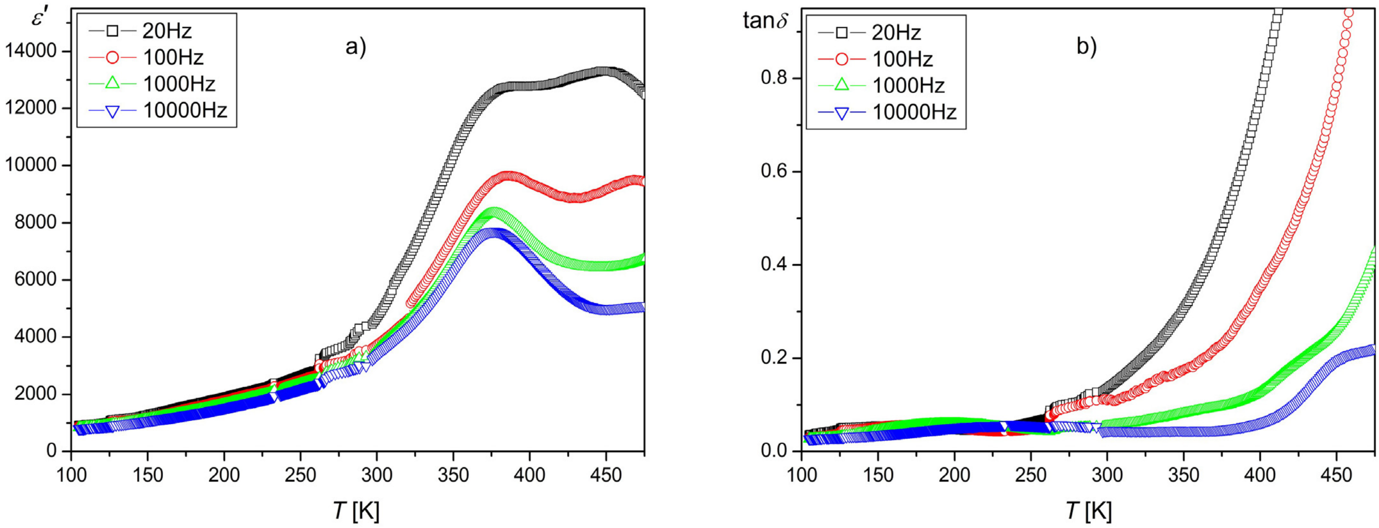

Fig. 6. Temperature dependencies of the dielectric permittivity (a) and tanδ (b) for the PFN ceramics

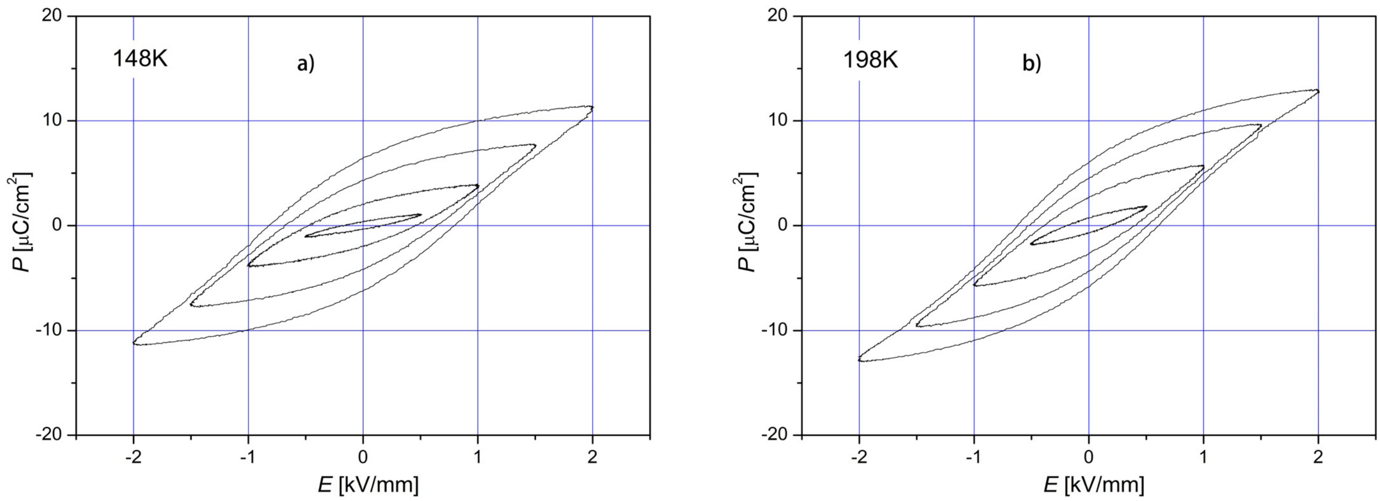

Fig. 7. $P(E)$ hysteresis loops at liquid nitrogen $T_1 < T_2 < T_3$ and in oil at teperatures higher than T_{room} (frequency of measuring field f =1 Hz)

same time there is no clear shift of temperature T_m with frequency of measuring field. At low temperatures the investigated PFN ceramics have low dielectric loss while at higher temperatures the values of the dielectric loss abruptly increase with increasing temperature.

The results of investigations of $P(E)$ hysteresis loops of investigated PFN ceramics at several temperatures (from 148K to 293K) are presented in Fig. 7. Increase in dielectric loss at higher temperatures leads to deformation the hysteresis loop. Remnant polarization has values from of 7 μC/cm^2 at 148K to 8.5 μC/cm^2 at 293K and a coercive field from 8 kV/cm at 148K to 5 kV/cm at 293K.

4. Conclusions

On X-ray diffraction patterns (at room temperature) of obtained PFN ceramics only the maxima related to the perovskite phase are visible, and there are no lines related with the other phases. The best fit was obtained for the pattern for the phase with tetragonal symmetry.

The microstructure of obtained PFN ceramics is fine-grained, and the grains are well-shaped. The average grain sizes of the investigated samples are about 1.3 μm. The temperature dependence of dielectric permittivity exhibits the influence of high electrical conductivity, especially at low frequencies and at high temperatures. The investigations of AC electric conductivity showed that at temperature range 240K-260K the anomalies of conductivity are observed which depend on measuring cycle (heating, cooling) and constant magnetic field. The results of investigations of $P(E)$ hysteresis loops of obtained PFN ceramics showed that at low temperatures the hysteresis loops are typical for ferroelectric materials. With increasing temperature the deformation of loops is visible what can be attributed to the increase of electric conductivity in PFN ceramics.

So we can say that the material with these properties can be used in modern micromechatronics and microelectronics for example in sensors and actuators.

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